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Statistical modelling of Thin Epoxy Resin Layers Curing Using Microwave Energy

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ABSTRACT

In this research microwave curing is used to support fast curing in order to prevent changes to the form and shape of a selective applied layer. In this investigation the layer consists of a liquid mixture of epoxy resin with aluminium particles is cured using microwave heating and is further used in rapid product development. The issue of statistical modelling of the fast curing process of thin epoxy resin layers using microwave heating is addressed in this paper. The modelling by a linear regression method is based on information available from the curing process as well as from data collected performing the Dynamic Scanning Calorimetry analysis. To reach the state of dimensional stability, the curing temperature of the layer material was controlled using two options. First, through the reduction of the microwave power and second, through altering the turntable speed so that the microwave exposure time of the layer was monitored. This operation was controlled using appropriate computer software.

1. INTRODUCTION AND BACKGROUND

The main objective of this study is to determine whether microwave heating could facilitate rate of curing of epoxy resins, thus achieving rapid solidification. Experiments were carried out to determine how quickly a thin layer of resin could be cured to the point that it is not flowing any more, which is important in the building a new product by using one of the rapid product development techniques. Curing is a result of exothermic reaction that increases the material's temperature, which in turn accelerates the curing. Therefore temperature change of a thin layer of resin exposed to a microwave field was measured. The temperature change was due to exothermic curing reaction and absorption of energy through interactions with microwave field.

Statistical models of the processes studied have been developed based on number of experiments designed by using statistical composite design of the experiments. Regression analysis has been used to determine relationships between the variables and the experimental outcome. In this case the variables were mixture composition of the resin, power of the microwave field applied and exposure time of the specimens to the microwave field. In all cases linear regression models using stepwise approach have been developed using SPlus software. The quality of all models was assessed using graphical diagnostic tools and descriptive estimates of the coefficients. The graphical diagnostic tool is a set of plots that summarises the basic statistical properties of the model derived from the data.

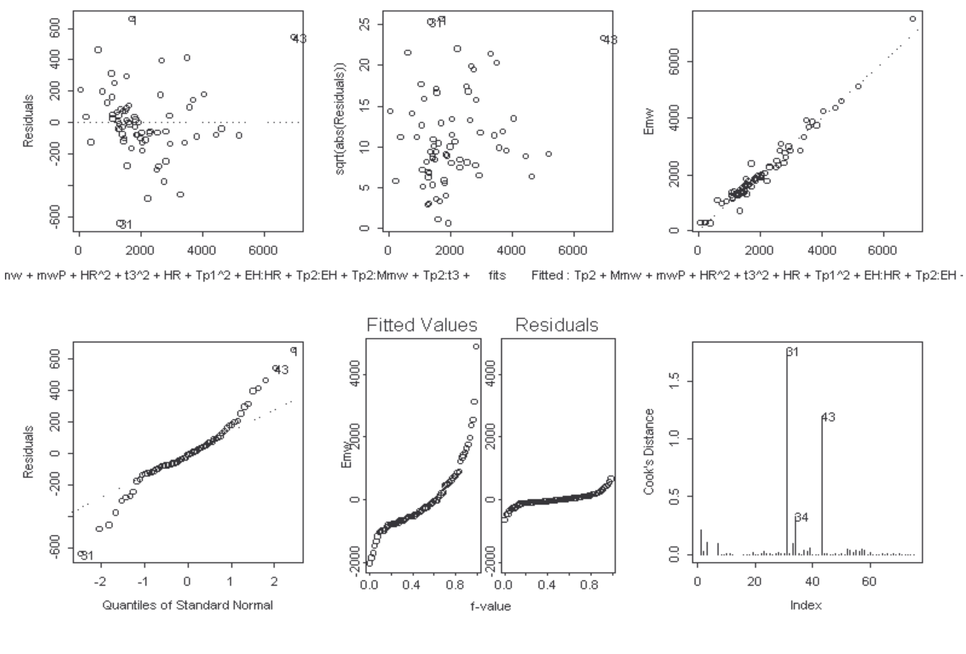


Figure 1: Example of diagnostic plots.

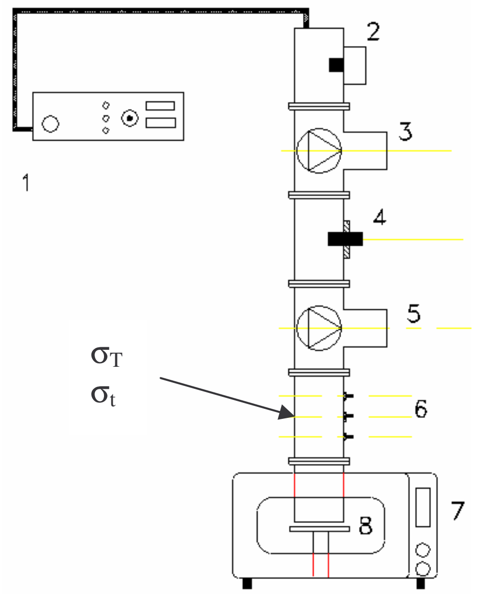
2. EXPERIMENTAL DETAILS

Specimens in the form of a thin layer of epoxy resin were exposed to a microwave field. The time of exposure and the mixture composition of the specimens are shown in Table 1. The microwave heating system used in these experiments is shown in Figure 2. Each sample was manually applied to a thin laboratory glass slide forming 0.4 to 0.55mm thick layer of epoxy resin. The specimen was placed 3mm below the tapered waveguide inside the microwave cavity, layed horizontally across a glass tube that was used as support structure. The surface temperature of each sample was measured using an IR thermopile that was positioned alongside the tapered waveguide. Figure 3 shows diagrammatically the temperature change (profile) of the specimen during the experiments.

Table 1: Summary of test-table includes mw-power, exposure time and mixture ratios.

Test No	MW-power (W)	Exp-time (sec)	Hardener (ml)	Aluminum (grams)	Resin (wt%)	Hardener (wt%)	Aluminum (wt%)
1	325	37.5	0.475	0.475	51.2	24.4	24.4
2	775	37.5	0.475	0.475	51.2	24.4	24.4
3	325	92.5	0.475	0.475	51.2	24.4	24.4
4	775	92.5	0.475	0.475	51.2	24.4	24.4
5	325	37.5	0.825	0.475	20.6	35.9	43.5
6	775	37.5	0.825	0.475	20.6	35.9	43.5
7	325	92.5	0.825	0.475	20.6	35.9	43.5
8	775	92.5	0.825	0.475	20.6	35.9	43.5
9	325	37.5	0.475	0.825	43.4	20.7	35.9
10	775	37.5	0.475	0.825	43.4	20.7	35.9
11	325	92.5	0.475	0.825	43.4	20.7	35.9
12	775	92.5	0.475	0.825	43.4	20.7	35.9
13	325	37.5	0.825	0.825	37.8	31.1	31.1
14	775	37.5	0.825	0.825	37.8	31.1	31.1
15	325	92.5	0.825	0.825	37.8	31.1	31.1
16	775	92.5	0.825	0.825	37.8	31.1	31.1
17	1000	65.0	0.650	0.650	43.4	28.3	28.3
18	550	120.0	0.650	0.650	43.4	28.3	28.3
19	550	65.0	1.000	0.650	37.7	37.7	24.6
20	550	65.0	0.650	1.000	37.7	24.6	37.7
21	100	65.0	0.650	0.650	43.4	28.3	28.3
22	550	10.0	0.650	0.650	43.4	28.3	28.3
23	550	65.0	0.300	0.650	51.3	15.4	33.3
24	550	65.0	0.650	0.300	51.3	33.3	15.4
25	550	65.0	0.650	0.650	43.4	28.3	28.3

The temperature was measured at the surface of the specimen. There are three distinctive stages. The first one reflects the rise of the specimen's temperature due to the heat transfer from the environment after the sample was placed in the microwave cavity. At this stage the sample's temperature increased during the time t_x. The area "E_{heat}" is proportional to the amount of heat absorbed. The value of E_{heat} varied with each experiment as the starting temperature varied. The manual tuning of the microwave system made it difficult to maintain, over time, the appropriate impedance resulting in loss of significant portion of the microwave energy, which affectively was diverted to heating the microwave system's hardware rather than the sample.



(1) Microwave power control unit,
(2) Magnetron,
(3) First circulator,
(4) Attenuator,
(5) Second circulator,
(6) Three stub tuner,
(7) Modified commercial microwave oven,
(8) Sample holder or modeling table.

Figure 2 Schematic diagram of microwave system for curing epoxy resin.

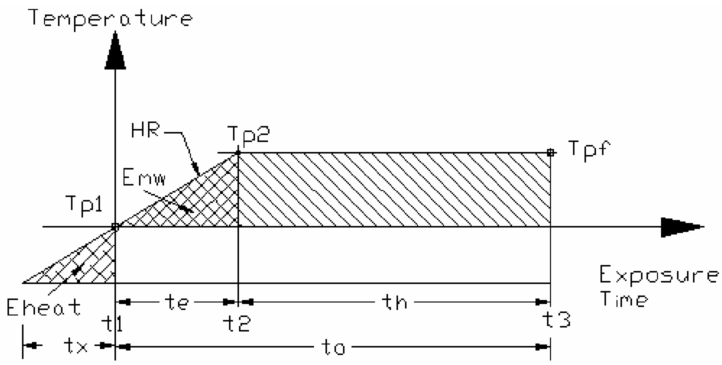


Figure 3 Temperature profile of microwave cured sample.

By continuously using the cavity for heating one specimen after the other, the temperature inside the cavity was gradually rising so the next sample placed in the cavity quickly absorbed heat to equilibrate the temperature. The time elapsed from placing the sample inside the cavity until starting the experiment was not recorded. However, it was estimated that it took on average approximately 10sec to the moment of commencing microwave heating. Thus the temperature T_{p1} was variable and the heat energy absorbed by the specimen prior to microwave exposure (E_{heat}) is proportional to:

$$E_{heat} \sim 1/2 \cdot t_x \cdot T_{pl} \qquad \text{(Eqn. 1)}$$

Where t_x is time of heating the specimen prior the microwave heating (sec) and T_{p1} is temperature at the beginning of the microwave exposure (°C).

The equation 1 describes the heat transfer to the specimen by conduction and radiation. Maintaining fixed temperature T_{p1} would require controlled cooling of the microwave cavity after each experiment.

The second stage starts at the temperature (T_{p1}) when the specimen is heated by microwave radiation until it reaches the predetermined maximum temperature (T_{p2}) of 240°C. The heat energy absorbed by the specimen is proportional to the area "E_{mw}":

$$E_{mw} \sim 1/2 \cdot (t_2 - t_1)(T_{p2} - T_{p1}) \qquad \text{(Eqn. 2)}$$

Where t_2, t_1 are finishing and starting time of microwave exposure (sec) and T_{p2}, T_{p1} are maximum and starting temperature of microwave exposure (°C)

Rise of the temperature from T_{p1} to T_{p2} over time t_e represents the heating rate (HR) of the specimen. This heating rate is determined by the interaction of the specimen with the microwave field, which in turn depends on mixture composition of the specimen. Thus HR should uniquely describe the reaction of specimens with the microwave field. Therefore E_{mw} that is proportional to microwave energy absorbed by the specimen can be described as follows:

$$E_{mw} \cong 1/2 \cdot HR \cdot t_e^2 \qquad \text{(Eqn. 3)}$$

Where HR is heat rate coefficient (°C/sec) and t_e is time of exposure (sec). The heat rate coefficient (HR) can be calculated using the data from the experiments.

The third stage relates to holding the temperature (T_{p2}) at a predetermined value of 240 °C. The experiments were designed based on mixture composition, exposure time and microwave power. It was found that in some cases specimens would be heated to high temperatures and burnt. To avoid this, at a predetermined temperature the microwave power was switched on and off to maintain constant temperature. The maximum temperature of 240°C was chosen after it was found that exposing the specimen up to 240°C for a limited period of time would not damage the material. The temperature was controlled by the IR-thermopile through switching the microwave power on and off. The microwave heat energy balanced the energy lost through radiation to the environment until the experiment was completed. After completing the experiment, the specimen was cooled rapidly and stored at -10°C in order to prevent further curing reactions.

3. MODELLING OF HEATING RATE COEFFICIENT

The following linear relationship has been determined.

$$\begin{aligned} HR = {} & 59.7 - 0.541 \cdot T_{p1} - 2.77 \cdot H + 0.02694 \cdot M_{mw} + 0.01359 \cdot H^2 + 0.01785 \cdot (T_{p1} \cdot H) \\ & + 8.3 \cdot 10^{-4} \cdot (mwP \cdot H) - 7.9 \cdot 10^{-4} \cdot (H \cdot M_{mw}) - 8.74 \cdot 10^{-6} (mwP \cdot M_{mw}) \\ & - 4.1 \cdot 10^{-4} \cdot (mwP \cdot Al) + 0.01205 \cdot (H \cdot Al) \end{aligned} \qquad \text{(Eqn. 4)}$$

Where HR is heating rate coefficient (°C/sec), T_{p1} is temperature of the specimen at the commencement of the microwave heating (°C), H is weight percent of hardener in the epoxy mixture (wt%), M_{mw} is mass of the specimen in grams, mwP is nominal microwave power applied in the experiment (W) and Al is weight percent of the aluminium powder in the mixture (wt%).

The diagnostic plot of the "Partial residual plot (top left) indicates a normal, independent distribution. The "Square root of absolute residuals against fitted values", (top centre) does not indicate a specific structure. There are some outliers but not of major influence to the regression model. The "Response versa the Fit" plot (top right) indicates the usefulness of the fit as a model. Most of the values are superimposed on the dotted line, indicating a normal distribution. The "Normal quantile plot of residuals" (bottom left) shows that the residuals are superimposed the zero mark (dotted line), indicating that the errors distribution is normal. The "Residual–Fit Spread or r-f plot" (bottom centre) shows the proportion of the variability between the fitted values and the residuals. In our case, the spread of the fitted values is larger than the residuals confirming that our model is valid. The "Cook's Distance" plot is useful for observation of individual regression coefficients. In this model there is no large value that would affect the model negatively and require isolation.

4. MODELING OF ABSORPTION OF MICROWAVE HEAT ENERGY

Following relationship for E_{mw} has been determined.

$$\begin{aligned} E_{mw} = {} & 50.1278 \cdot T_{p2} - 9.005 \cdot M_{mw} + 55.9499 \cdot HR^2 + 0.2425 \cdot t_h{}^2 \\ & - 1506.9196 \cdot HR + 0.1727 \cdot T_{p1}{}^2 + 1.311 \cdot (EH \cdot HR) - 0.0822 \cdot (T_{p2} \cdot EH) \\ & + 0.0365 \cdot (T_{p2} \cdot M_{mw}) + 0.0014 \cdot (mwP \cdot t_h) - 0.1015 \cdot (T_{p2} \cdot t_h) \end{aligned} \qquad \text{(Eqn. 5)}$$

Where E_{mw} is proportional to microwave heat energy absorbed by the specimen, HR is heating rate coefficient (deg/sec), EH is area proportional to energy absorbed by the specimen due to microwave exposure, t_h is time during which the temperature was held constant (sec), T_{p1} is temperature of the specimen at the commencement of the microwave heating (°C),T_{p2} is temperature of the specimen at the end of the microwave heating (°C), M_{mw} is mass of the specimen in grams, mwP is nominal microwave power applied in the experiment (W).

Analysing the diagnostic plots at the "absolute residuals against fitted values" (top left) identifies values that do not fit inside the visualised structure of the residuals. The plot "Square root of absolute residual against fitted values" (top centre) compares the spread of the fitted values with the spread of the residuals. The distribution of values identifies some concentration that could have an affect on our result. The plot of “quantities of standard normal-residuals” (left bottom) superimposes the zero or normal distribution line of model errors. The plot of “partial residual” (top right) confirms the linearity and has indicated some incompatible residuals. The “Cook’s distance plot” (right bottom) reflects that most of the values have been useful for the regression model, and also reflects the standard deviation. In both regression models the heat rate HR-model is based on variables, however, the absorption of microwave produced heat energy E_{mw} includes in the structure the heat rate function (HR) and therefore makes the E_{mw} function more complex. The relationship between the absorbed microwave produced heat energy and the heat rate over exposure time (t_e) is graphically presented in Figure 4.

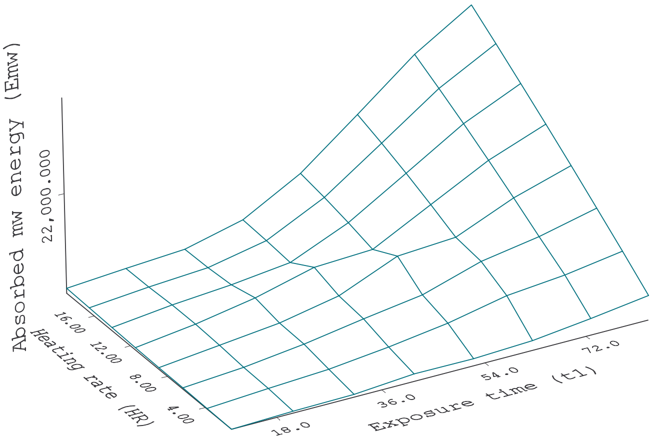


Figure 4 3-D plot of curing epoxy samples using microwave energy.

Figure 4 indicates that microwave energy is absorbed over time and converted into heat (E_{mw}). The absorption of microwave energy progresses exponentially with the square of the exposure time. Analysing the model of the heat rate coefficient (HR), it was noticed that five variables are important. These five variables were used as single values and in combination to develop the model shown for the heat rate (HR). The important variable, absolute value, is the hardener (H) with 82%, followed by the starting temperature (T_{p1}) with 16%. The variables such as mass of specimen, aluminum content and microwave power share the remaining 2% of the HR-model. The absorbed microwave heat energy (E_{mw}) is a combination of the heat rate (HR) and additional variables as shown in the model. Most of the model parameters are not material related, where the main contribution comes from the heat rate (HR) followed by the final temperature (T_{p2}) and the mass of the specimen (M_{mw}) with 7.7%, together they share 98.3% of the model. The starting temperature (T_{p1}) which was still an important variable for modeling (HR) slipped to 0.15% and hardly contributes to the E_{mw}-model. The rest of variables participate in combination at the absorbed microwave heat energy (E_{mw}) and achieved about 1.7% of the model.

5. CALCULATION OF MICROWAVE EXPOSURE

The mathematical analysis of microwave heating involves equations that are coupled to Maxwell’s equations of electromagnetic radiation. This has been discussed in the following section, including the application of both models. The method of volumetric heating applied through microwaves is a unique form of processing material following the Maxwell’s equation. The closest conventional heating method equivalent to microwave heating is the method of ‘transient heat flow in systems with negligible internal resistance’, under the assumption that the internal thermal resistance of the system is low and that the temperature at any point of the system is uniform through thermal diffusion. Based on the analytical modelling performed in this chapter, we know that the heat rate (HR) multiplied with the exposure time (t_e) will cure a layer of epoxy resin. The heat energy absorbed by the sample that is proportional to the microwave energy, was calculated in the following paragraph under the assumption of no heat loss to the environment. The heating process of any material is represented in equation 6.

$$-c_p \cdot \rho \cdot VdT = \bar{h} \cdot A_s \cdot (T - T_o) \cdot d\theta \qquad \text{(Eqn. 6)}$$

Where c_p is specific heat of dielectric(J/kg°K), V is volume of the dielectric(m^3), h is average heat transfer coefficient (J/m^2 sec °K), A_s is surface area of dielectric(m^2), T, T_0 are temperature change (°C) and dθ is time factor at temperature change(sec).

We consider that the temperature within a material is substantially constant at any instant and the energy balance over a small time period is zero. Microwave energy is converted into heat by the dielectric material property at a temperature rate following distinct parameters. The relationship between the microwave power (P) and the amount of heat (Q_h) produced over time (t) is presented in the equation 7

$$P = \frac{Q_h}{t} = M_a c_p (T - T_o) / t \qquad (W) \qquad \text{(Eqn.7)}$$

Where P is power(W), Q_h is amount of heat(kJ) and t is time(sec)

The temperature rate is calculated using the following equation [7]:

$$(T - T_o) / t = \frac{0.556 \cdot 10^{-10} \varepsilon''_{eff} f E^2_{rms}}{\rho c_p} \qquad (°C/sec) \qquad \text{(Eqn. 8)}$$

Where M_a is mass of dielectric(kg), c_p is specific heat(kJ/kg°C), T is final temperature (°C), T_o is starting temperature (°C), and ε''_{eff} is affective loss factor (farad/m). The power consumed by the dielectric material can be calculated using the temperature difference versa the time factor, as indicated in equation 6.8. This calculation, however, presents an average value of the power consumption consumed by the dielectric material. For a more accurate calculation we should consider the electric field strength before calculation of the average power consumption

5. CONCLUSIONS

The outcome of the models confirms a close relationship between thermodynamic equations of transient heat flow in systems with negligible internal resistance (see Equation.6) and analytical modelling presented in two regression models such as the heating rate (HR) and the microwave energy absorbed (Emw). It can be observed that over the exposure time the heat of the sample increases, based on the heat rate over exposure time. Finally, the epoxy resin mixture is cured at the glass transition temperature. The intention was to design and develop a new technique of fast curing the material mixtures using microwave heating. A modified industrial microwave oven was used as a resonant cavity with a speed controlled turntable as a modelling platform. The microwave energy was supplied by a specially designed applicator to enhance the electric field strength. The epoxy resin was sprayed onto a rotating platform close to the microwave applicator. Curing of the epoxy layer was performed while a layer was exposed to the microwave electromagnetic field shortly after application. A major part of this research is focused on determining the optimal material combination to enable fast curing. To this end it was important to generate an extensive experimental data set in order to understand the relationship between microwave power, exposure time and the material for fast curing. Therefore, a special waveguide was designed to cure samples of epoxy resin amine mixtures. In order to understand and to specify the curing state of microwave exposed samples, samples were analysed using Dynamic Scanning Calorimetry. In line with the curability of epoxy resin amine layers, the material properties of layer mixtures were investigated by conducting tensile and hardness tests.

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